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## Nanoscale titanium dioxide $(nTiO_2)$ transport in water-saturated sand columns: Influence of phosphate, illite colloid, and Fe-oxyhydroxide coating

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Nanoscale titanium dioxide (nTiO<sub>2</sub>) is an important emerging contaminant due to its mass production in recent years. While extensive research has been performed using simplified laboratory systems to study the stability and transport of nTiO2, much fewer investigations are conducted to examine the behaviour of nTiO2 in complicated systems similar to natural aquifers with heterogeneous transport media and multiple water-borne components. To better understand the fate and transport of nTiO<sub>2</sub> in natural environments, we performed laboratory column experiments to measure nTiO<sub>2</sub> transport in water-saturated sand columns in the co-presence of multiple components including dissolved phosphate, suspended illite colloid, and Fe-oxyhydroxide coating on sand grains. Results showed that pH plays a crucial role in how phosphate, illite colloid, and Fe-oxyhydroxide coating influence nTiO<sub>2</sub> transport. At pH 5 in the absence of phosphate and illite colloid, despite favorable deposition conditions, nTiO<sub>2</sub> was found in the effluent of the quartz column after  $\sim$ 4.5 PV (pore volume) due to saturation of deposition sites, after which effluent nTiO2 concentration quickly increased and then levelled off. For the Fe-oxyhydroxide coated sand column under the same conditions, whereas the shape of the BTC (breakthrough curve) was similar to that for the quartz sand column,  $nTiO_2$  was detected in the effluent much earlier ( $\sim 1$  PV), owing to the reduction in favorable deposition sites caused by Fe-oxyhydroxide coating. When illite colloid was co-present with nTiO2 in the influent at pH 5, nTiO $_2$  concentration in the effluent gradually increased to C/C0 =  $\sim$ 0.08 and  $\sim$ 0.22 respectively for the quartz sand and Fe-oxyhydroxide coated sand columns. The low transport was attributed to physical straining caused by formation of the nTiO<sub>2</sub>-illite aggregates during the experiment. For all the experiments with phosphate in the influent at pH 5, nTiO<sub>2</sub> was not detected in the effluent regardless of the presence of illite colloid or Fe-oxyhydroxide coating, presumably due to straining of the large nTiO<sub>2</sub> aggregates formed via phosphate bridging. At pH 9, for both the quartz sand and Fe-oxyhydroxide coated sand columns with or without phosphate, high nTiO<sub>2</sub> transport was observed for all but one experiment. The high transport was due to the repulsive forces between nTiO2 and the transport media. For the Fe-oxyhydroxide coated sand column without phosphate or illite colloid at pH 9, nTiO<sub>2</sub> transport was considerably lower (C/C0 ~0.07), as a result of pH buffering by the Feoxyhydroxide coating, which made the Fe-oxyhydroxides positively charged, and therefore providing favorable sites for nTiO<sub>2</sub> deposition. This study demonstrated that common water-borne components and minerals in transport media could significantly alter nTiO2 transport and the interactions between each component and nTiO2 as well as the synergy effects of these components must be considered in order to predict the behaviour of nTiO2 in natural environments.